

Equilibrium Studies in the System $\text{AgBr}-(\text{K},\text{Na})\text{Br}-(\text{K},\text{Na})\text{NO}_3$
at 280°C and the Significance of Solvation Effects in the
Interpretation of Data on Silver Halide Complexation in
Nitrate Melts.

BERTIL HOLMBERG

Division of Physical Chemistry, Lund University, Chemical Center,
P.O.B. 740, S-220 07 Lund, Sweden.



The distribution of NaBr between a solid solution (Ag,Na)Br and fused equimolar (K,Na)NO₃ has been studied at 280 °C. The activities of AgBr and NaBr in the solid have been determined from the distribution data and the stability constants for the complexes AgBr₂⁻, AgBr₃²⁻ and Ag₂Br₆⁴⁻ in the nitrate melt calculated. As compared to previous conventional solubility measurements the present study gives the same general picture of the complex formation, although the magnitudes of the stability constants for AgBr₃²⁻ and Ag₂Br₆⁴⁻ are increased as the solid solubility is taken into account. The activities of AgBr and NaBr in the solid may be roughly rationalized according to a regular solution model and the estimated interaction parameter, 9 kJ mol⁻¹, compares well with results obtained by other methods.

The influence of variations in the nitrate ion activity on the interpretation of data in terms of complex formation reactions between silver and halide ions has been analysed. An exchange in the silver ion coordination sphere of nitrate for halide ions does not generally influence the over-all qualitative picture of the complexation, although the stability constants exhibit a slight change in magnitude as compared to the case of the more common model of interpretation, where changes in the solvent activity are ignored. It is, however, demonstrated that effects that have been previously ascribed to the presence of AgI₄³⁻ in minor amounts may be eliminated by taking into account solvation of the "free" silver ion by nitrate ions.

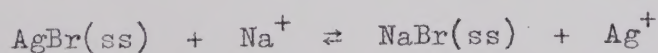
The rôle of solid solution formation in solubility studies on silver halide complex formation in nitrate melts has been treated in two recent papers,^{1,2} where the solubility and distribution of α -AgI between solid and liquid solutions was investigated. An earlier paper from this laboratory reported results from a study of the stepwise formation of silver bromide complexes AgBr , AgBr_2^- , AgBr_3^{2-} and $\text{Ag}_2\text{Br}_6^{4-}$ in $(\text{K}, \text{Na})\text{NO}_3$ at 280°C .³ In the latter study the conventional solubility method was utilized in the concentration range $0.001 \text{ mol kg}^{-1} \leq \underline{C}_{\text{Br}} \leq 2 \text{ mol kg}^{-1}$, and the results were compared with those from previous potentiometric work.⁴

Later, Sinistri and Pezzati⁵ performed similar solubility measurements in this system at 275°C and 300°C in the range $0.001 \text{ mol kg}^{-1} \leq \underline{C}_{\text{Br}} \leq 0.5 \text{ mol kg}^{-1}$ and determined the stability constants for AgBr , AgBr_2^- and AgBr_3^{2-} . The constitution of the solid bromide phase was not checked in either of the investigations.³⁻⁵

It is well known, however, that AgBr and NaBr are completely miscible in the solid state at elevated temperatures.⁶⁻⁹ The existence of a miscibility gap was predicted by Kleppa and Meschel¹⁰ and this prediction was later confirmed by high temperature X-ray diffraction studies.⁷⁻⁹ The upper critical solution temperature has been reported to be 280°C ,⁷ around 330°C ⁸ and 285°C .⁹

The system AgBr-KBr is a simple eutectic one, and no solid solutions have been reported.^{6,11}

Since molten nitrate solutions have proved to be efficient in equilibrating solid α -AgI with alkali iodide, the experimental part of this study was undertaken in order to find out if a solid-liquid ion exchange reaction



is of importance in the solubility studies, and to elucidate the influence on the interpretation of the data concerning the stability of the silver bromide complexes in the nitrate phase. Furthermore, in the system AgBr-NaBr the thermodynamics of the solid solution formation have been studied previously by different methods, such as calorimetry,¹⁰ emf measurements⁸ and miscibility gap investigations.⁹ Therefore, this system is suitable in testing the applicability of the approach to the solid solution-nitrate melt distribution data, which will be presented in this paper.

The application of the thermodynamic model to the nitrate melt, makes it possible to calculate the nitrate ion activity.

This in turn means that it might perhaps be meaningful to make a conceptual distinction between "free" nitrate ions and those attached to a silver ion in the coordination sphere of a solvated central ion. In melts rather concentrated in halide ions, where the thermodynamic activity of the solvent changes markedly as the concentrations of solutes are changed, it might therefore be of significance to regard the complex formation equilibria strictly as a reversible exchange of solvent ions coordinated to the central ion for ligand ions, producing "free" solvent ions. Hence, the variable nitrate activity should be taken into account in the definition of equilibrium constants. The bearing of this "solvation effect" on the interpretation of complex formation data in melts concentrated in ligand ions will be tested on the present experimental material and on previous data on silver iodide complexation in iodide-rich alkali nitrate melts.^{1,14}

EXPERIMENTAL

Chemicals. Silver nitrate, sodium nitrate and potassium nitrate (Merck, p.a.) were pretreated as described previously.¹² Potassium

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41553216_0024

bromide and sodium bromide (Merck, p.a.) were dried at 140°C for several days prior to use. Silver bromide was prepared from hot aqueous solutions of AgNO_3 and KBr .

Apparatus. Large Pyrex test tubes were used as reaction vessels. They were thermostated in a closely fitting aluminium block, which was carefully thermally insulated and furnished with tubes for occasional illumination and observation of the melts. The systems were agitated by vigorous stirring with a Pyrex propeller. A fast cycling regulator, type CR/DHS/PID/SCR from Eurotherm, Worthing, England controlled the temperature of the system, which was kept at $(280.08 \pm 0.02)^{\circ}\text{C}$ (IPTS-68).

Procedure. In the main experiments (series A) systems containing 7.50 g AgBr , 75.00 g equimolar $(\text{K},\text{Na})\text{NO}_3$ and various amounts of equimolar $(\text{K},\text{Na})\text{Br}$ were equilibrated at 280°C . Equilibration times of 12 h were shown to be sufficient, but all systems were as a rule run for at least 24 h. Samples from the nitrate phase were then withdrawn, quenched and analysed for bromide and silver (in the range $\frac{C_{\text{Br}}}{\text{mol kg}^{-1}} \geq 1$).

In another experimental series (B) the equilibrium was approached by precipitating the solid AgBr phase in systems originally containing 6.78 g AgNO_3 , 70.57 g $(\text{K},\text{Na})\text{NO}_3$ and various amounts of $(\text{K},\text{Na})\text{Br}$.

In separate experiments it was ascertained that no loss of bromide could be detected when systems $(\text{K},\text{Na})\text{NO}_3 - (\text{K},\text{Na})\text{Br}$ were equilibrated at 280°C for even ten days or more. It was also checked that variations in the amount of solid AgBr relative to $(\text{K},\text{Na})\text{NO}_3$ had no influence on the experimental results.

The study was restricted to the range $0.1 \text{ mol kg}^{-1} \leq \underline{C}_{\text{Br}} \leq 2 \text{ mol kg}^{-1}$.

Analyses. The silver content of melts with $\underline{C}_{\text{Br}} \geq 1 \text{ mol kg}^{-1}$ was determined by electroanalytical precipitation on a rotating platinum cathode from hot aqueous cyanide solutions. For systems with $\underline{C}_{\text{Br}} < 1 \text{ mol kg}^{-1}$ sufficiently accurate values of $\underline{C}_{\text{Ag}}$ were obtained by interpolation in the solubility curve determined by Cigén and Mannerstrand.³ The alkali bromide content of the melts was determined by titration with standard AgNO_3 solution on samples suspended in water. The endpoint was detected potentiometrically.

The composition of the solid phase was calculated from the difference between added and found amounts of alkali bromide in the nitrate melt.

RESULTS AND DISCUSSION

The following notations and symbols will not be specifically defined in the text:

For the solid phase ($i = 1$ for AgBr and 2 for NaBr):

$\underline{x}_i$ = mole fraction of component $\underline{i}$.

$\underline{a}_i$ = activity of component $\underline{i}$.

$\underline{f}_i = \underline{a}_i \underline{x}_i^{-1}$

For the nitrate melt:

All concentrations are expressed in molality units mol kg^{-1} , referring to equimolar $(\text{K,Na})\text{NO}_3$ as solvent.

$\underline{C}_{\text{Br}}, \underline{C}_{\text{Ag}}, \underline{C}_0$ = total concentrations of bromide, silver and nitrate, respectively.

$$\begin{aligned}
[A] &= \text{concentration of species A.} \\
a(A) &= \text{activity of species A.} \\
\beta_{nm} &= [Ag_{\underline{m}}Br_{\underline{n}}^{(\underline{m}-\underline{n})}][Ag^+]^{-\underline{m}}[Br^-]^{-\underline{n}} \\
\underline{M}, \underline{N} &= \text{maximum value of } \underline{m} \text{ and } \underline{n}, \text{ respectively.} \\
\frac{x_o}{x_o} &= \frac{c_{Ag}}{c_{Ag}}[Ag^+]^{-1}. \\
\frac{x_{\underline{n}}}{x_{\underline{n}}} &= (\frac{x_{\underline{n}-1}}{x_{\underline{n}-1}} - \beta_{(\underline{n}-1)1})[Br^-]^{-1} ; \beta_{01} = 1. \\
\frac{\bar{n}}{\bar{n}} &= (\frac{c_{Br}}{c_{Br}} - [Br^-])\frac{c_{Ag}}{c_{Ag}}^{-1}. \\
K'_1 &= [Ag^+][Br^-]a_1^{-1}.
\end{aligned}$$

For the sake of clarity the treatment of data will at first be described without considering the "solvation effect", referred to in the introduction.

The complex formation in the nitrate melt.

Following a previously published calculation method,¹ we would have determined the activity a_1 of AgBr in the solid from the equations

$$d \ln a_1 = -(\frac{x_2}{x_1}) d \ln a_2 \quad (1)$$

$$d \ln a_2 = d \ln ([Na^+][Br^-]) \quad (2)$$

However, the use of molality concentrations for ionic species, which are common with the solvent, in expressions such as eqn. (2) may be criticized from a thermodynamic point of view.

Consider a nitrate melt with the ion constituents K^+ , Na^+ , NO_3^- , Br^- , Ag^+ and complexes $Ag_{\underline{m}}Br_{\underline{n}}^{(\underline{m}-\underline{n})}$. Since activities of all solute species are expressed as concentrations on the molality scale - which lies inherent in the complex formation model used - the Gibbs-Duhem equation may be written for the nitrate melt as (P and T are constant)

$$\begin{aligned}
& [K^+] d \ln \underline{a}(K) + [Na^+] d \ln \underline{a}(Na) + [NO_3^-] d \ln \underline{a}(NO_3) + \\
& + [Br^-] d \ln [Br^-] + [Ag^+] d \ln [Ag^+] + \\
& + \sum_{\underline{m}=1}^{\underline{M}} \sum_{\underline{n}=1}^{\underline{N}} [Ag_{\underline{m}} Br_{\underline{n}}^{(\underline{m}-\underline{n})}] d \ln [Ag_{\underline{m}} Br_{\underline{n}}^{(\underline{m}-\underline{n})}] = 0
\end{aligned} \quad (3)$$

Applying the stoichiometric requirements

$$\underline{C}_{Br} = [Br^-] + \sum_{\underline{m}=1}^{\underline{M}} \sum_{\underline{n}=1}^{\underline{N}} \underline{n} [Ag_{\underline{m}} Br_{\underline{n}}^{(\underline{m}-\underline{n})}] \quad (4)$$

$$\underline{C}_{Ag} = [Ag^+] + \sum_{\underline{m}=1}^{\underline{M}} \sum_{\underline{n}=1}^{\underline{N}} \underline{m} [Ag_{\underline{m}} Br_{\underline{n}}^{(\underline{m}-\underline{n})}] \quad (5)$$

and the equilibrium conditions

$$d \ln [Ag_{\underline{m}} Br_{\underline{n}}^{(\underline{m}-\underline{n})}] = \underline{m} d \ln [Ag^+] + \underline{n} d \ln [Br^-] \quad (6)$$

to eqn. (3) we obtain

$$\begin{aligned}
& [K^+] d \ln \underline{a}(K) + [Na^+] d \ln \underline{a}(Na) + [NO_3^-] d \ln \underline{a}(NO_3) + \\
& + \underline{C}_{Br} d \ln [Br^-] + \underline{C}_{Ag} d \ln [Ag^+] = 0
\end{aligned} \quad (7)$$

If, however, $\underline{a}(K)$, $\underline{a}(Na)$ and $\underline{a}(NO_3)$ are substituted with molality concentrations and eqn. (7) is combined with eqns. (1) and (2), we obtain the following equation for nitrate melts in equilibrium with $(Ag,Na)Br(s)$:

$$\begin{aligned}
& [K^+] d \ln [K^+] + ([Na^+] - \underline{x}_2 \underline{x}_1^{-1} \underline{C}_{Ag}) d \ln [Na^+] + \\
& + (\underline{C}_{Br} - \underline{x}_1^{-1} \underline{C}_{Ag}) d \ln [Br^-] = 0
\end{aligned}$$

This is obviously a false expression, since all terms of the left hand member will be of positive sign as the $(K,Na)Br$ concentration is increased. Hence, no support can be found for the use of $[Na^+]$ in eqn. (2). Since K^+ and Na^+ are the only cations present in the nitrate melt ($[Ag^+]$ is negligible in these alkali bromide containing melts), and since the $K:Na$ molar balance exhibits very small variations

in these melts, it is felt that more realistic expressions for $d \ln a(\text{Na})$ and $d \ln a(\text{K})$ would be $d \ln y$ and $d \ln(1-y)$, respectively, where

$$y = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+]) \quad (8)$$

The activity a_1 is then obtained (cf. Ref. 1) by

$$a_{1j} = \exp \left[\int_{\ln R_0}^{\ln R_j} \left(\frac{x_2}{x_1} \right) d \ln R \right] \quad (9)$$

where

$$R = (y[\text{Br}^-])^{-1} \quad (10)$$

and R_0 indicates a value of R in a system with $x_2 = 0$. The index j is used to denote corresponding values of different quantities referring to the same actual system. Since the experimental data do not extend to $x_2 = 0$, the integration according to eqn. (9) was started at $[\text{Br}^-] = 0.0988 \text{ mol kg}^{-1}$. The quantities so determined ($\ln a_1([\text{Br}^-]_j) - \ln a_1(0.0988 \text{ mol kg}^{-1})$) were plotted vs. $[\text{Br}^-]$ and the smooth curve obtained was easily extrapolated to $[\text{Br}^-] = 0$ to yield $a_1(0)/a_1(0.0988 \text{ mol kg}^{-1})$. All activities a_{1j} were then calculated setting $a_1(0) = 1$ (cf. Ref. 13), and the concentration product $([\text{Ag}^+][\text{Br}^-])_j$ has been computed as $K'_1 a_{1j}$. In doing so we used the value $K'_1 = 3.00 \times 10^{-7} (\text{mol kg}^{-1})^2$ which was potentiometrically determined by Cigén and Mannerstrand⁴ and which was used in their calculation of stability constants from solubility data.³ The results are all collected in Table 1.

In the composition range investigated, AgBr_2^- , AgBr_3^{2-} and $\text{Ag}_2\text{Br}_6^{4-}$ appear to be the predominant complexes. The function X_2 was calculated by use of β_{11} from Ref. 3, and β_{21} was easily obtained as the limiting value $\lim_{[\text{Br}^-] \rightarrow 0} X_2$. Since X_3 was found to vary linearly with $[\text{Ag}^+][\text{Br}^-]^3$, the constants β_{31} and β_{62} were determined from the linear relationship

$$\underline{x}_3 = \underline{\beta}_{31} + 2\underline{\beta}_{62}[\text{Ag}^+][\text{Br}^-]^3 \quad (11)$$

All calculations were iterated until no significant change in the parameters could be observed.

When the solid solubility of NaBr in AgBr is taken into consideration, the over-all picture of the complexation is on the whole left unaffected as compared to previous findings.^{3,5} As can be seen from Table 2 the value of $\underline{\beta}_{21}$ is not influenced, whereas a slight increase in $\underline{\beta}_{31}$ and a still more pronounced increase in $\underline{\beta}_{62}$ is obtained when the variable composition of the solid phase is accounted for.

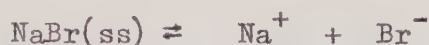
It is noteworthy that the discrepancies between the potentiometrically determined values of $\underline{\beta}_{31}$ and $\underline{\beta}_{62}$ and those obtained from solubility data increase as the solid solution formation is accounted for in the calculations. It is also to be noted that the potentiometrically determined product $[\text{Ag}^+][\text{Br}^-]$ seems to increase as $\underline{C}_{\text{Br}}$ increases in the region $\underline{C}_{\text{Br}} > 1.00 \text{ mol kg}^{-1}$,⁴ whereas our analysis of the distribution data indicates a decrease in $[\text{Ag}^+][\text{Br}^-]$ due to the lowering of the AgBr activity in the solid. These two discrepancies are consistent with each other in the sense that they may both be "explained" by assuming too large apparent values of $[\text{Ag}^+]$ from the emf-data due to liquid junction potentials in those melts which are concentrated in $(\text{K}, \text{Na})\text{Br}^-$ - provided that halide containing melts exhibit the same ideal thermodynamic behaviour as liquid $\text{AgNO}_3 - (\text{K}, \text{Na})\text{NO}_3$ systems.¹²

For the sake of comparison we calculated the activities $\underline{a}_1$ according to eqns. (1) and (2) as well. The maximum difference in $\underline{a}_1$, as compared to the values of Table 1, amounts to less than 1% and there is no change in the determined values of the stability constants. A check of the data pertaining to silver iodide complexes¹ gave similar results, i.e. the choice of model for the change of the alkali metal ion activities

is of little importance as long as only the complex equilibria in the nitrate melt are considered. The present approach, however, appears to be thermodynamically more sound.

The solid solution (Ag,Na)Br.

The activities $\underline{a}_2$ for NaBr in the solid have been calculated as follows. According to eqn. (8) an equilibrium constant $\underline{K}'_2$ for the reaction



is defined as

$$\underline{K}'_2 = \underline{\gamma}[\text{Br}^-] \underline{a}_2^{-1} \quad (12)$$

A polynomial approximation is made, viz.

$$\underline{x}_2 / (\underline{\gamma}[\text{Br}^-]) = \sum_{i=0}^2 \underline{b}_i \underline{x}_2^i \quad (13)$$

and, following a method previously described,¹ $\underline{a}_2$ is determined as

$$\underline{a}_2 = \underline{b}_0 \underline{\gamma}[\text{Br}^-] \quad (14)$$

since $\underline{b}_0$ may be identified as $\underline{K}'_2{}^{-1}$. From a least-squares analysis $\underline{K}'_2 = (9 \pm 1) \text{ mol kg}^{-1}$ with the error expressed as three standard deviations. The standard states for NaBr in the solid and for Na^+ in the nitrate melt are chosen to be in accordance with the conditions $\lim_{\underline{x}_2 \rightarrow 0} \underline{f}_2 = 1$ and $\underline{a}(\text{Na}) = \underline{\gamma} = 0.500$ in pure equimolar $(\text{K,Na})\text{NO}_3(1)$, respectively. The values of $\underline{a}_2$ and $\underline{f}_2$ are included in Table 1.

Kleppa and Meschel¹⁰ measured the enthalpy of mixing of AgBr and NaBr at 350 °C. Extending their rationalization of data into the dilute solution region $0.05 \leq \underline{x}_2 \leq 0.20$ we obtain a two-parameter equation

$$\frac{RT}{\text{mol}} \ln \underline{f}_1 = \underline{A} \underline{x}_2^2 + \underline{B} \underline{x}_2^3 \quad (15)$$

Tsuji and coworkers⁸ fitted emf data to the regular solution expression

$$\underline{RT} \ln \underline{f}_1 = \underline{A} \underline{x}_2^2 \quad (16)$$

Based on miscibility gap calculations, a two-parameter model analogous to eqn. (15) was proposed by Sinistri and coworkers.⁹ The data of both Kleppa and Sinistri can, however, be effectively described by a one-parameter regular solution model, eqn. (16), in our dilute solution region.

Our experimental data ($\underline{f}_1$; $\underline{x}_2$) are well described by eqn. (16) in the range $0.046 \leq \underline{x}_2 \leq 0.200$. A value of $\underline{A}$ may also be derived from the $\underline{f}_2$ data. With the present choice of standard state for NaBr in the solid solution the expression consistent with eqn. (16) is

$$\underline{RT} \ln \underline{f}_2 = \underline{A}(\underline{x}_1^2 - 1) \quad (17)$$

The values of $\underline{A}$ calculated from literature data are given in Table 3 together with those from this study. The good agreement with previous results indicates that the present method of analysing complex equilibria in melts which are equilibrated with solid solutions of variable composition yields reliable values of the activities of the components in the solid phase.

The nitrate ion activity

The present approach to the problem of deriving reliable values of $\underline{a}_1$ leads to a complete model description of the nitrate melt in terms of ion activities, since $\underline{a}(\text{NO}_3^-)$ is determined by eqn. (7). For the two first terms in the left hand member of this equation we have

$$[\text{K}^+] d \ln (1 - \underline{y}) + [\text{Na}^+] d \ln \underline{y} = 0 \quad (18)$$

Hence, a general expression for the nitrate ion activity is

$$d \ln a(\text{NO}_3) = -\underline{C}_0^{-1} (\underline{C}_{\text{Br}} d \ln [\text{Br}^-] + \underline{C}_{\text{Ag}} d \ln [\text{Ag}^+]) \quad (19)$$

Furthermore, for systems investigated in this study

$$d \ln [\text{Ag}^+] = -\underline{x}_1^{-1} (\underline{x}_2 d \ln \underline{y} + d \ln [\text{Br}^-]) \quad (20)$$

and eqn. (7) then yields

$$d \ln a(\text{NO}_3) = \underline{C}_0^{-1} [(\underline{C}_{\text{Ag}} \underline{x}_1^{-1} - \underline{C}_{\text{Br}}) d \ln [\text{Br}^-] + \underline{C}_{\text{Ag}} \underline{x}_2 \underline{x}_1^{-1} d \ln \underline{y}] \quad (21)$$

In the present case the second term of the right hand member of eqn. (21) is negligible. Setting $a(\text{NO}_3) = 1$ in pure $(\text{K}, \text{Na})\text{NO}_3$ (1), the nitrate ion activity may be computed according to

$$a(\text{NO}_3)_1 = \exp \left[\int_{-\infty}^{\ln [\text{Br}^-]_1} \underline{C}_0^{-1} (\underline{C}_{\text{Ag}} \underline{x}_1^{-1} - \underline{C}_{\text{Br}}) d \ln [\text{Br}^-] \right] \quad (22)$$

In the calculation the solubility data of Ref. 3 were utilized in the dilute solution range. The resulting nitrate activities are included in Table 1. The Table thus contains thermodynamically self-consistent values of activities and concentrations according to the model used, which may be schematically summarized as follows:

- a. For Ag^+ , Br^- and complexes $\text{Ag}_{\underline{m}}\text{Br}_{\underline{n}}^{(\underline{m}-\underline{n})}$ the activities are approximated by concentrations in molality units.
- b. For Na^+ and K^+ the activities are taken to be $\underline{y}$ and $1-\underline{y}$, respectively, with $\underline{y} = [\text{Na}^+] / ([\text{Na}^+] + [\text{K}^+])$.
- c. For NO_3^- the activity is expressed through $d \ln a(\text{NO}_3) = -\underline{C}_0^{-1} (\underline{C}_{\text{Br}} d \ln [\text{Br}^-] + \underline{C}_{\text{Ag}} d \ln [\text{Ag}^+])$. The reference state is pure equimolar $(\text{K}, \text{Na})\text{NO}_3$ (1) with $a(\text{NO}_3) = 1$.

The influence of variable nitrate ion activity on the interpretation of data.

In complex formation studies the solvent activity is generally regarded as constant, an assumption which is justified by the fact that only very dilute solutions are studied. In the present case, however, $a(\text{NO}_3) = 0.83$ in melts with $C_{\text{Br}} = 2.2 \text{ mol kg}^{-1}$ as compared to $a(\text{NO}_3) = 1$ in the pure solvent. The situation is also rather similar in silver iodide systems which have been investigated previously.^{1,14}

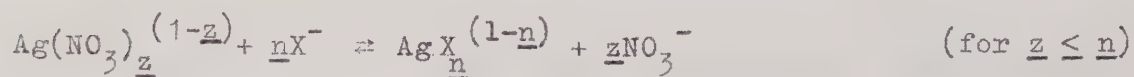
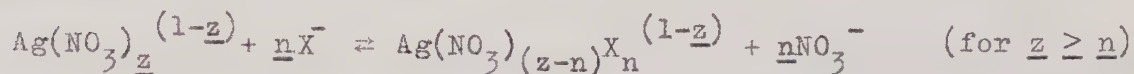
In calculations aiming at identification of complex species and determination of their thermodynamic stabilities the formation equilibria have been represented as



However, from vibrational spectra studies conclusive evidence for strong interaction between silver and nitrate ions in pure AgNO_3 melts as well as molten alkali metal nitrate - silver nitrate mixtures has emerged.¹⁵⁻²⁷ Recently, Clarke and Hartley,²⁶ in an enlightening study of the features of the low frequency silver nitrate Raman band at 107 cm^{-1} , concluded that specific ionic association between silver and nitrate ions is of significance in such melts. Particularly interesting was the observation that substitution of 20 % of the nitrate ions by halide ions in a mixed silver caesium nitrate melt resulted in a decrease in the band intensity of about 40 %. This implies that the formation of silver halide complexes in an alkali metal nitrate melt should rather be regarded as a ligand exchange reaction, the halide ions replacing nitrate ions in the coordination sphere of silver to produce "free" nitrate ions.

The lack of precise information on the nature of the nitrate solvated silver ion and the mechanism of halide complexation (and even the real over-all composition of the species formed by a total or partial replacement of nitrate by halide), limits our examination of the effects of variations in the solvent activity to the use of a very simple model for the complex formation.

For the sake of simplicity the calculations will be restricted to two model cases with $\underline{z} = 2$ and 4, assuming that the over-all formation equilibria can be represented as

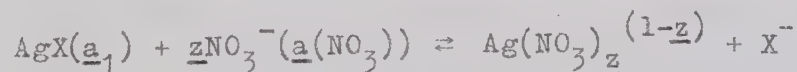


and



This means that effects such as possible changes from bidentate nitrate ions to monodentate as a halide ion enters the coordination sphere (e.g. no "free" nitrate ion is produced) are not accounted for in the model although such mechanisms for the complex formation might very well be of significance. As for $\text{Ag}_2\text{X}_6^{4-}$, it is supposed that silver is coordinatively saturated in the dinuclear complex.

The AgX distribution equilibrium between the solid halide phase and the nitrate melt



and hence

$$[\text{Ag}^+][\text{X}^-] = \underline{K}'_1 \underline{a}_1 \underline{a}(\text{NO}_3)^{\underline{z}} \quad (23)$$

For the case of a liquid halide phase an analogous expression is easily derived. The over-all stability constants for the complex formation reactions should be defined as

$$\beta_{n1}^* = [\text{AgX}_n]^{(1-n)} \underline{a}(\text{NO}_3)^{\underline{n}} [\text{Ag}^+]^{-1} [\text{X}^-]^{-\underline{n}} \quad (\text{for } \underline{z} \geq \underline{n}) \quad (24)$$

$$\beta_{n1}^* = [\text{AgX}_n]^{(1-n)} \underline{a}(\text{NO}_3)^{\underline{z}} [\text{Ag}^+]^{-1} [\text{X}^-]^{-\underline{n}} \quad (\text{for } \underline{z} < \underline{n}) \quad (25)$$

$$\beta_{62}^* = [\text{Ag}_2\text{X}_6]^{4-} \underline{a}(\text{NO}_3)^{2\underline{z}} [\text{Ag}^+]^{-2} [\text{X}^-]^{-6} \quad (26)$$

In (23) - (26) and all following expressions the possibility of solvated anions has been disregarded, since it has no bearing on the interpretation of the data.

It is easily shown that a very good approximation of the general expression for the nitrate ion activity is (cf. eqn. (19))

$$d \ln \underline{a}(\text{NO}_3) = -(\underline{C}_0 - \underline{C}_X + [\text{X}^-])^{-1} (\underline{C}_X d \ln[\text{X}^-] + \underline{C}_{\text{Ag}} d \ln[\text{Ag}^+]) \quad (27)$$

for $\underline{z} \geq \underline{n}$. (A slight and numerically unimportant modification occurs for $\underline{z} < \underline{n}$.) The expression corresponding to eqn. (22) is then

$$\underline{a}(\text{NO}_3)_{\underline{j}} = \exp \left[\int_{-}^{\ln[\text{X}^-]_{\underline{j}}} (\underline{C}_0 - (\underline{n} - \underline{z})\underline{C}_{\text{Ag}})^{-1} (\underline{C}_{\text{AgX}_1}^{-1} - \underline{C}_X) d \ln[\text{X}^-] \right] \quad (28)$$

An analysis of the experimental data pertaining to the present AgBr solubility study according to eqns. (23) - (28) reveals that the effects of nitrate solvation do not change the conclusion concerning what complex species exist in the melt. The β^* -values are given in Table 4. From a comparison with Table 2 it is seen that only moderate changes in the constants are obtained when the present solvation model is applied.

A similar check of the silver iodide solubility data of Ref. 1 was performed under the two previous assumptions¹ that either AgI_3^{2-} , AgI_4^{3-} and $\text{Ag}_2\text{I}_6^{4-}$ (alternative I) or only AgI_3^{2-} and $\text{Ag}_2\text{I}_6^{4-}$ (alternative II) are the predominating silver containing species in iodide-rich nitrate melts. The results are collected in Table 5. Like the bromide case there is no significant change in the results as $\underline{z}$ is assumed to take integer values from zero to four.

Finally, the weak indication of the presence of AgI_4^{3-} as it appeared from potentiometric data¹⁴ obtained in unsaturated melts was checked. The evaluation of β_{31} and β_{41} from the f_4^0 -function (defined in Ref. 14) was re-examined on the basis of eqns. (24) - (26) for $\underline{z} = 2$ and 4. The nitrate activity is difficult to obtain from the general expression (27) since the integration path is a priori indetermined. It was assumed, however, that $\underline{a}(\text{NO}_3)$, to a good approximation, is a function of $[\text{I}^-]$ only and hence the data for saturated melts were utilized to yield $\underline{a}(\text{NO}_3)$ values for the proper values of $[\text{I}^-]$ by means of numerical interpolation. The data processing produces values of β_{31} which are on the whole the same for different $\underline{z}$, viz. $(2.2 \pm 0.1) \times 10^7 (\text{mol kg}^{-1})^{-3}$. The value of β_{62} decreases somewhat as $\underline{z}$ is increased from zero $((1.2 \pm 0.3) \times 10^{16} (\text{mol kg}^{-1})^{-7}$ for $\underline{z} = 2$ as compared to $(1.9 \pm 0.7) \times 10^{16} (\text{mol kg}^{-1})^{-7}$ for $\underline{z} = 0$), whereas β_{41} is effectively zero or apparently slightly negative for $\underline{z} = 2$ and 4.

From the present examination of the solvation effect it becomes evident that the interpretation of potentiometric data is brought into a qualitative agreement with solubility and distribution data as interpreted according to alternative II, if the nitrate solvation of $\text{Ag}(\text{I})$ is considered. This means that effects that have been ascribed to the presence of AgI_4^{3-} might very well have their origin in the liberation of NO_3^-

ions from the solvated silver ions as the iodide complexation proceeds. A more precise quantitative evaluation of the "solvation effect" can not be made, since the detailed mechanisms of the complex formation processes are unknown.

In conclusion, the results may be summarized in the following way. Considering complex species which account for fairly large fractions of the total central ion concentration, the "solvation effect" has probably no bearing on the data interpretation in the sense that the apparent composition of the complexes is unaffected by variations in the solvent activity of about 20 % or less, provided a reasonable degree of solvation of the uncomplexed central ion is assumed. The magnitudes of the corresponding stability constants are also remarkably uninfluenced by the choice of $\underline{z}$ (including $\underline{z} = 0$). It seems, however, that serious misinterpretation of data might result, if species present in only minor amounts are considered in melts where the solvent activity changes significantly.

Acknowledgements. I thank Professor Ido Leden for many inspiring discussions. Fil.mag. Göran Thomé skilfully assisted in the experimental work. I also thank Dr. Peter Sellers for the linguistic revision of the manuscript.

REFERENCES

1. Holmberg, B. Acta Chem. Scand. 27 (1973) 3657.
2. Holmberg, B. Acta Chem. Scand. 27 (1973) 3550.
3. Cigén, R. and Mannerstrand, N. Acta Chem. Scand. 18 (1964) 2203.
4. Cigén, R. and Mannerstrand, N. Acta Chem. Scand. 18 (1964) 1755.
5. Sinistri, C. and Pezzati, E. Gazz. Chim. Ital. 97 (1967) 1116.
6. Zemczuzny, S.F. Z. Anorg. Allg. Chem. 153 (1926) 47.
7. Wynnyckyj, J.R., Schmalzried, H. and Sockel, H.-G. Z. Phys. Chem. (Frankfurt am Main) 68 (1969) 30.
8. Tsuji, T., Fueki, K. and Mukaibo, T. Bull. Chem. Soc. Jpn. 42 (1969) 2193.
9. Sinistri, C., Riccardi, R., Margheritis, C. and Tittarelli, P. Z. Naturforsch. Teil A 27 (1972) 149.
10. Kleppa, O.J. and Meschel, S.V. J. Phys. Chem. 69 (1965) 3531.
11. Bradley, J.N. and Greene, P.D. Trans. Faraday Soc. 63 (1967) 424.
12. Holmberg, B. Acta Chem. Scand. A 28 (1974) 284.
13. Johansson, L. Acta Chem. Scand. A 28 (1974) 708.
14. Holmberg, B. Acta Chem. Scand. 27 (1973) 875.
15. Janz, G.J. and James, D.W. J. Chem. Phys. 35 (1961) 739.
16. Wilmschurst, J.K. and Senderoff, S. J. Chem. Phys. 35 (1961) 1078.
17. Walrafen, G.E. and Irish, D.E. J. Chem. Phys. 40 (1964) 911.
18. Janz, G.J. and Kozlowski, T.R. J. Chem. Phys. 40 (1964) 1699.
19. Wait, S.C., Ward, A.T. and Janz, G.J. J. Chem. Phys. 45 (1966) 133.
20. Wait, S.C. and Ward, A.T. J. Chem. Phys. 44 (1966) 448.
21. Devlin, J.P., Williamson, K. and Austin, G. J. Chem. Phys. 44 (1966) 2203.
22. Li, P. and Devlin, J.P. J. Chem. Phys. 49 (1968) 1441.
23. Vallier, J. J. Chim. Phys. Phys.-Chim. Biol. 65 (1968) 1762.
24. James, D.W. and Leong, W.H. J. Chem. Phys. 51 (1969) 640.

25. Clarke, J.H.R. Chem. Phys. Lett. 4 (1969) 39.
26. Clarke, J.H.R. and Hartley, P.J. J. Chem. Soc. Faraday Trans. 2
68 (1972) 1634.
27. Kawamura, K. Trans. Japan Inst. Metals 16 (1975) 281.

Table 1. Experimental data and calculated quantities. Values of $\underline{C}_{Ag}$ which are taken from Ref. 3, are printed in italics. Solvation of silver ions is ignored.

Series	$\frac{C_{Br}}{(\text{mol kg}^{-1})}$	$\frac{C_{Ag}}{(\text{mol kg}^{-1})}$	χ	$\frac{[Na^+]}{(\text{mol kg}^{-1})}$	χ_1	$\frac{a_1}{f_1}$	$\frac{a_2}{f_2}$	$\frac{[Br^-]}{(\text{mol kg}^{-1})}$	$\frac{[Ag^+][Br^-] \times 10^7}{(\text{mol kg}^{-1})^2}$	$\frac{a(NO_3)}{a(NO_3)}$		
A	0.1009	<u>0.0010</u>	0.500	5.421	0.994	0.998	1.004	0.006	1.0	0.998	2.99	0.991
A	0.1952	<u>0.0021</u>	0.500	5.466	0.989	0.993	1.004	0.011	1.0	0.1903	2.98	0.982
A	0.3906	<u>0.0055</u>	0.499	5.560	0.978	0.981	1.003	0.021	1.0	0.3768	2.94	0.964
B	0.3971	<u>0.0056</u>	0.499	5.563	0.980	0.983	1.003	0.021	1.0	0.3829	2.95	0.963
A	0.591	<u>0.0111</u>	0.499	5.653	0.963	0.971	1.008	0.032	0.86	0.562	2.91	0.947
A	0.807	<u>0.0187</u>	0.499	5.750	0.954	0.959	1.005	0.042	0.91	0.756	2.88	0.929
B	0.991	0.0262	0.499	5.839	0.938	0.949	1.012	0.052	0.84	0.918	2.85	0.914
A	0.991	0.0261	0.498	5.838	0.937	0.948	1.012	0.051	0.81	0.919	2.84	0.914
A	0.994	0.0261	0.498	5.841	0.939	0.949	1.011	0.052	0.85	0.922	2.85	0.914
A	1.241	0.0399	0.498	5.952	0.921	0.933	1.013	0.063	0.80	1.129	2.80	0.896
B	1.256	0.0410	0.498	5.961	0.928	0.940	1.013	0.064	0.89	1.140	2.82	0.895
A	1.498	0.0571	0.498	6.066	0.896	0.917	1.023	0.075	0.72	1.343	2.75	0.877
A	1.502	0.0562	0.498	6.069	0.897	0.919	1.024	0.075	0.73	1.337	2.76	0.877
A	1.758	0.0774	0.497	6.179	0.867	0.901	1.039	0.086	0.65	1.537	2.70	0.860
A	2.023	0.1010	0.497	6.295	0.846	0.882	1.042	0.097	0.63	1.732	2.65	0.843
B	2.029	0.1023	0.497	6.300	0.853	0.890	1.043	0.097	0.66	1.732	2.67	0.843
A	2.221	0.1236	0.496	6.371	0.800	0.867	1.084	0.104	0.52	1.862	2.60	0.832

Table 2. A comparison between stability constants obtained by different methods.

Investigation and method	$\beta_{21}/(\text{mol kg}^{-1})^{-2}$	$\beta_{31}/(\text{mol kg}^{-1})^{-3}$	$\beta_{62}/(\text{mol kg}^{-1})^{-7}$
<u>Potentiometric measurements</u>			
Ref. 4, 280 °C			
Unsaturated melts	$(2.4 \pm 0.1) \times 10^4$	$(5.9 \pm 0.7) \times 10^4$	$(1.2 \pm 0.6) \times 10^{10}$
<u>Solubility studies</u>			
Ref. 5, 275 °C			
Solid solubility ignored	2.4×10^4	7.8×10^4	-
Ref. 3, 280 °C			
Solid solubility ignored	2.3×10^4	6.7×10^4	2.2×10^{10}
This study, 280 °C			
Solid solubility accounted for; $1 \leq \alpha_1 \leq 0.87$.	2.3×10^4	$(7.0 \pm 0.4) \times 10^4$	$(3.0 \pm 0.4) \times 10^{10}$
Solvation effects ignored.			

Table 3. Different values of the regular solution parameter $\underline{A}$, estimated in the region of dilute solid solutions of NaBr in AgBr.

Ref.	Method	Temperature	$\underline{A}/(\text{kJ mol}^{-1})$
10	Enthalpy of mixing	350 °C	8 ± 1
8	Emf of the cell	350 °C	
	Ag/(Ag,Na)Br(s)/Br ₂	400 °C	10 ± 1
9	Miscibility gap studies	280 °C	9 ± 2
This study	Distribution measurements	280 °C	
	$\underline{RT} \ln \underline{f}_1 / \underline{x}_2^2$		11 ± 2
	$\underline{RT} \ln \underline{f}_2 / (\underline{x}_1^2 - 1)$		7 ± 2

Table 4. Apparent stability constants of silver bromide complexes for various silver(I) solvation numbers z.

<u>z</u>	$\beta_{31}^* \times 10^{-4} / (\text{mol kg}^{-1})^{-3}$	$\beta_{62}^* \times 10^{-10} / (\text{mol kg}^{-1})^{-7}$
2	7.0 ± 0.3	2.9 ± 0.3
4	7.8 ± 0.4	3.3 ± 0.3

Table 5. Apparent stability constants of silver iodide complexes for various silver(I) solvation numbers $\bar{z}$.
Experimental solubility data and other details are given in Ref. 1.

		Alternative I. ¹			Alternative II. ¹		
$\bar{z}$		$\beta_{31}^* \times 10^{-7} / (\text{mol kg}^{-1})^{-3}$	$\beta_{41}^* \times 10^{-7} / (\text{mol kg}^{-1})^{-4}$	$\beta_{62}^* \times 10^{-16} / (\text{mol kg}^{-7})^{-7}$	$\beta_{31}^* \times 10^{-7} / (\text{mol kg}^{-1})^{-3}$	$\beta_{62}^* \times 10^{-16} / (\text{mol kg}^{-1})^{-7}$	
0	(Ref. 1)	2.4 ± 0.3	3.6 ± 0.7	1.6 ± 0.7	3.8 ± 0.6	3.1 ± 0.6	
2		2.5 ± 0.3	3.8 ± 0.7	1.4 ± 0.6	3.8 ± 0.5	3.4 ± 0.5	
4		2.6 ± 0.3	4.0 ± 0.7	1.3 ± 0.6	4.0 ± 0.5	3.6 ± 0.5	

